

EFFECT OF ENERGETIC MATERIALS ON THE THERMAL STABILITY OF POLYMERS

A. S. TOMPA

Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910

ABSTRACT

The effect of energetic additives such as ammonium perchlorate, ammonium persulfate, cyclotetramethylenetetranitramine, triaminoguanidine nitrate, plastisol nitrocellulose, and a nitrate lacquer at the 5% level had on the thermal stability of polyacetals, aliphatic and aromatic polyesters, and polyamides was investigated by isothermal and dynamic thermogravimetry in a nitrogen and air atmosphere. Activation energies were determined for some of the admixtures; the additives were found to lower the activation energy by 30 to 88%. The effect of a series of ammonium and potassium salts on the thermal degradation of polyacetals was determined. It was found that the more acid character the cation and anion moieties had, the more effective the substance was in decreasing the thermal stability of polyacetals. Thermal instability of an admixture of polymer and additive was observed as a shift of the thermogravimetry curve to a lower temperature or by an increase in the rate of volatilization. Dynamic thermogravimetry studies of polyacetal admixtures offered a novel method for distinguishing between the acid strengths of the additives.

INTRODUCTION

The objective of this study was the development of thermally decomposable structural materials and the effect of energetic additives on the thermal stability of these materials. Such polymeric materials should decompose at temperatures somewhat above their processing temperatures, which should not be too high and leave little or no residue. The materials should be dimensionally stable in humid environments and should be sufficiently rigid so that thin-walled containers can be prepared from them. The additives should significantly lower the decomposition temperature and residue if any of the structural material. The practical addition of these additives to polymeric systems that may be used in the fabrication of consumable cartridge cases would not be during the melt process because of the potential for degradation occurring; rather it could be applied to the finished

product in the form of an aerosol spray after the surface to be coated is abraded which would increase the surface area and thereby the burning rate.

EXPERIMENTAL

Commercial polymers investigated included polyacetals (Delrin, Celcon), polyester (Hytrel, Valox, Lucite), and polyamides (Nylons 4, 612). Energetic additives included ammonium persulfate (APS), ammonium perchlorate (AP), cyclotetramethylene-tetranitramine (HMX), triaminoguanidine nitrate (TAGN), plastisol nitrocellulose (PNC), and a black lacquer coating (BLC) which contained cellulose nitrate. Nonenergetic additives included ammonium and potassium inorganic salts, and eleven organic compounds which yielded free radicals of carbon, nitrogen, oxygen, sulfur, and halogen.

From 4 to 5 mg of additive was added to 90 to 100 mg of powdered polymer and the mixture was ground in a Wig-L-Bug for one minute to insure uniform distribution. Aliquots of about 5 mg were used. Isothermal thermogravimetry (TG) was carried out at 305^o, 355^o, and 424^oC in a nitrogen and air atmosphere on a DuPont 990 thermal analyzer with a 951 thermogravimetric module. Dynamic thermogravimetry studies were run at a heating rate of 5 or 15^oC/minute. Dynamic differential scanning calorimetry (DSC) studies were carried out in a sealed pan with a pin-hole in the cover at a heating rate of 5^oC/minute.

DISCUSSION

The effect of metal catalysts on the oxidative degradation of rubbers has been investigated by many workers and has been reviewed by Dunn (ref. 1). Reich (ref. 2) studied the compatibility of polymers with highly energetic materials in the ratio of nearly 1:1 by weight using DSC. Cagliostro (ref. 3) etc. studied the effect of citric acid on Delrin using TG. Swanson and Madsen (ref. 4) evaluated the compatibility of three propellants with a variety of plastic adhesives and foams using DSC.

Thus thermoanalytical techniques such as TG and DSC have been shown to be powerful tools for investigating the thermal stability of mixtures of polymeric materials and energetic additives.

A very useful thermal analytical technique for following the degradation of polymers is isothermal thermogravimetric analysis. The fraction of material remaining at a given temperature as a function of time is determined. The data are analyzed by plotting the rate of volatilization (% per minute) as a function of the volatilization. Theoretical analysis of these isothermal curves for polymer degradation studies (refs. 5-6) show the following observations: (1) a maximum rate at ca. 25% volatilization is found for pure random depolymerization or for depolymerization of moderate zip length involving considerable molecular transfer; (2) a maximum at ca. 50% volatilization is representative of depolymerizations in

which the initiation occurs at chain ends, the zip length is moderate and either a slight amount of transfer or random initiation takes place; (3) the maxima of the isothermal curves may be taken as the rate constants for the calculation of activation energies for the reactions involved in the degradation; (4) a straight line parallel to the abscissa means that the degradation reaction follows zero order kinetics, and may be observed when depolymerization is initiated at chain ends and the zip length is much shorter than the polymer chain length; (5) a straight line inclined to the abscissa indicates a first order reaction and may be observed when the zip length is much larger than the polymer chain length; and (6) the maximum rate shifts towards lower conversion as the reaction order increases.

Activation energies were calculated for the thermal decomposition of Celcon and Lucite and for some of their admixtures (Table 1). The additives were found to lower the activation energy by 30 to 88%. Doyle's (ref. 7) relationship between isothermal and dynamic TG was used by plotting $\Delta(\log t)_{i50}$ versus $\Delta(1/T)_{dyn}$ at fixed conversion values (α), a slope of 0.457 E/R was obtained (Figure 1). Wall's (ref. 8) method for isothermal TG was used by plotting $\Delta(\log t)_{i50}$ versus $\Delta(1/T)_{i50}$ at constant α values, a slope of 0.457 E/R was obtained.

Isothermal Polymer Degradation

Table 2 gives the rate of volatilization of the polymers at 355°C in nitrogen and air. The order in air is Celcon > Delrin > Lucite >> Nylon 4 >> Hytrel Valox > Nylon-612. Rate of volatilization plots are shown in Figures 2 and 3. Delrin in Figure 2 shows only a plateau at 305°C in nitrogen and a straight line plot in air, a maxima at about 60 to 70% at 355°C, and a shift in the maxima to a higher percent volatilization as the temperature is raised to 424°C. These results indicate that different processes are occurring at different temperatures in nitrogen and air. In Figure 3, it is seen that Celcon and Lucite have their rate of volatilization maxima at about 20 to 40% while for Hytrel it is at 50% volatilization.

The effect of energetic additives on the thermal degradation of polymers at 355°C in nitrogen and air is given in Tables 3 to 9. Dynamic TG in Figures 4 and 5 show the effect of these additives on Delrin and Celcon respectively.

Polyethers: Delrin and Celcon

Delrin is an acetal homopolymer and Celcon is an acetal copolymer. The data in Tables 3 and 4 show that the rate of volatilization is greater in air than in nitrogen. The following observations are evident for Delrin namely (1) the order for the effect of additives in increasing the rate of volatilization in nitrogen or air is: AP > PNC > APS >> HMX > TAGN = BLC; (2) in nitrogen there are maxima in the rate of volatilization only with BLC, TAGN, and Delrin by itself; and (3) in air there is a monotonic increase in the rate of volatilization for Delrin with/without additives. With Celcon it is seen that (1) in nitrogen the order is AP > APS >> BLC > PNC > HMX > TAGN; (2) in air the order is APS > AP >

HMX > PNC > TAGN >> BLC; (3) in nitrogen there are peak maxima in the rate of volatilization with HMX, TAGN, PNC, BLC, and Celcon by itself (4) in air there is a monotonic increase in the rate of volatilization for Celcon with/without additives. The dynamic TG curves in Figures 4 and 5 show the same order for the effectiveness of the additives except that APS > AP with Delrin.

Thus Delrin by itself has a greater rate of volatilization in nitrogen than Celcon by itself, while in air they are nearly the same. The most effective additives in increasing the rate of volatilization of Delrin and Celcon are APS and AP, the effect is about the same in air while in nitrogen it is slightly greater for Delrin. Table 1 shows that APS and PNC decreased the activation energy for the thermal decomposition of Celcon by 88 and 75% respectively.

Polyesters: Hytre1, Valox, and Lucite

Hytre1 is a terephthalate copolymer, Valox a terephthalate polymer, and Lucite an aliphatic polymethylmethacrylate. Tables 5, 6 and 7 show that energetic additives have an insignificant effect on the rate of volatilization of Hytre1 and Valox whether in a nitrogen or air atmosphere, and a great effect on Lucite especially in an air atmosphere. Hytre1 and Valox show peak maxima in their rate of volatilization. Hytre1 has a slightly higher volatilization in air than in nitrogen, and it is a little more than that for Valox. The order for the additives in increasing the rate of volatilization for Hytre1 is (1) in nitrogen, BLC > AP > APS >> HMX = PNC > TAGN, (2) in air, BLC > AP = APS > PNC > HMX > TAGN; for Valox in nitrogen or air it is BLC > AP = APS = HMX = TAGN = PNC. However for Hytre1 or Valox with/without additives their rate of volatilization at 355°C in nitrogen or air is very low compared to that for Delrin, Celcon, and Lucite.

For Lucite the order for the additives in increasing the rate of volatilization in nitrogen is AP >> HMX > TAGN > APS > PNC = BLC. In air the rate of volatilization is much greater and the order is AP = HMX = TAGN > APS = PNC >> BLC >> Lucite. Lucite by itself has a greater rate of volatilization in air than in nitrogen. In nitrogen, Lucite with/without additives shows a peak maxima in the rate of volatilization while in air there is a monotonic increase in the rate. Table 1 shows that AP and NH₄Cl decreased by 71 and 30% respectively, the activation energy required for the thermal decomposition of Lucite. Figure 6 shows the effect of the AP concentration on the thermal decomposition of a mixture of Lucite + AP. The limiting effect is at about 2% AP.

Polyamides: Nylon 4 and Nylon 612

Table 8 shows the effect of additives on the rate of volatilization of Nylon 4 at 355°C in nitrogen and air. A peak maxima in the rate of volatilization was not observed in nitrogen or air. The rate of volatilization is about the same in nitrogen or air for Nylon 4 with/without additives except for AP. The order for the additives is: AP > APS = HMX = TAGN = PNC = BLC = Nylon 4.

Nylon 612 had a much lower rate of volatilization at 355°C, it was lower than that for Hytrel or Valox.

Volatilization Order for Additives

In nitrogen at 355°C the volatilization order for the energetic additives was: PNC > TAGN > HMX > APS > AP. The first three volatilized in less than 0.8 minutes, APS in 10.6 minutes, and AP in 46 minutes. In air, PNC and HMX volatilized faster, APS and TAGN a little slower, and AP about the same as in nitrogen. Thus one of the advantages of APS and AP as additives was the longer time that they are effective in promoting the breakdown of polymers, especially polyacetals.

The Effect of Free Radical Initiators on the Thermal Decomposition of Delrin

The effect of eleven additives yielding free radicals of carbon, nitrogen, oxygen, sulfur and halogen on the thermal degradation of Delrin was investigated. The following order of effect on lowering the decomposition temperature was observed: N-bromosuccinimide >> peracetic acid-40% > N-chlorosuccinimide > dicumyl peroxide > azoisobutyronitrile > dimethyl benzylamine > benzoyl peroxide > 1,3-diphenyltriazene > paramenthane hydroperoxide > tertiary butyl hydroperoxide -70% > tetramethyl thiuram disulfide. The more effective additives had exotherms in the melting region (170-190°C) of Delrin. Combination of free radical initiators with ammonium persulfate or ammonium perchlorate had only a small synergistic effect; it was greater with ammonium persulfate. The order among the additives are summarized in Table 10 by listing the temperatures at which 80% decomposition by weight occurs. The most effective organic free radical initiator was found to be N-bromosuccinimide (C₄H₄O₂NBr). It caused a two-step TG curve with the first step complete at 152°C after a 35% weight loss (Figure 7). The substitution of bromine for a chlorine atom in N-halosubstituted succinimide causes a large, dramatic effect on the decomposition of Delrin. Perhaps, it should not be too surprising that N-bromosuccinimide reacts differently since it is known from kinetic studies in the gas phase between hydrogen and halogen that with chlorine a simple second order reaction is found, while with bromine a complex reaction order expression is obtained. The dynamic TG curves in Figure 7 show the effect of some of the additives on the thermal decomposition of Delrin.

Ammonium persulfate and N-bromosuccinimide are the most effective free radical initiators studied so far in lowering the decomposition temperature of Delrin. This may be because their exotherms come in the melting range of Delrin, and consequently, because of the liquid phase you can have a greater interaction. However, 1, 3 diphenyltriazene, also has an exotherm in the 180° - 200°C region and it is not an effective additive. Perhaps, because of its low melting point and consequently, possible mass losses due to vaporization, that its effective concentration may be low in the processing range of Delrin. DSC curves are shown in Figure 8.

Effect of Halide Salts on Delrin

Figure 9 shows the effectiveness of ammonium and potassium halides on lowering the decomposition temperature of Delrin. The order is $\text{NH}_4\text{I} > \text{NH}_4\text{Br} > \text{NH}_4\text{Cl} > \text{KI} > \text{KBr}$. This trend among the halides may be correlated with the increase in covalent character, ionic radius, acidity, and atomic number of the halogen as you go down Group VIIA. In comparing cations with non-metal and metal properties, $\text{NH}_4 > \text{K}$ because the nitrogen atom in ammonium is more electronegative than potassium and therefore is less basic or has more acidic character.

Figure 10 shows the effect of chloride salts of zinc, aluminum and ammonium on the decomposition of Delrin and Celcon. The observed order is $\text{Zn} \gg \text{NH}_4 > \text{Al}$. Zinc chloride has the most deleterious effect on the stability of Delrin and Celcon. Over 50% decomposition occurs before the melting point, with degradation starting at $\sim 40^\circ\text{C}$. It leaves a 4.8% residue at 300°C in a nitrogen atmosphere, while in air there is a 7.5% residue at 300°C which decreased to 2% at 500°C . Zinc chloride has a synergistic effect on the decomposition of polyacetals since zinc acetylacetonate or other chloride salts do not have such a dramatic effect. It affects Celcon and Delrin to approximately the same extent. Hybart and Rowley (ref. 9) found that zinc stearate and zinc chloride accelerated the degradation of polyvinyl chloride because of the catalytic action of zinc chloride. Grassie and McGuchan (ref. 10) observed that zinc chloride appears to be more efficient than strong acids in the catalytic degradation of polyacrylonitrile.

Effect of Perchlorates on Celcon

Figure 11 shows the effect of perchlorates on the decomposition of Celcon. The decomposition order is $\text{NH}_4 > \text{Mg} > \text{Li} > \text{K} > \text{Cs}$. In an overly simplified manner, this trend may be correlated with changes in the values of ionic potential (charge/radius), oxidation potentials and acidity as you go down and across the Periodic Table. Decreasing covalent character is predicted with increasing atomic number in groups containing metals and the opposite in groups containing nonmetals.

In Group 1a, the smaller cation (Li) because of its greater concentration of positive charge has a greater polarizing effect upon an anion than a larger cation (Cs) and thus favors increasing covalent character with increasing ionic potential ($\text{Mg} > \text{Li} > \text{K} > \text{Cs}$). In addition, as the size of the cation decreases, its oxidation potential decreases ($\text{Mg} < \text{K} < \text{Cs}$; Li is anomalous) and its acidity increased. Thus the decomposition order of perchlorates may be explained on the basis of increasing acidity and covalent character of the cations ($\text{NH}_4 > \text{Mg} > \text{Li} > \text{K} > \text{Cs}$) as you go up a group (1a) and across a period in the Periodic Table. Osawa (ref. 11) postulated that the more ionic character there is in a metallic salt, the more effective it is for the catalyzed thermal oxidative degradation of isotactic polypropylene.

Effect of Ammonium Perchlorate Concentration on Celcon and Delrin

Figure 12 shows the effect of NH_4ClO_4 concentration on the decomposition of Celcon and Delrin. The addition of only 0.2% AP causes a dramatic decrease in the thermal stability of polyacetals. Increasing the AP concentration beyond 0.4% has only a negligible effect on the decomposition of Delrin and Celcon and that Celcon and Delrin are affected to the same extent. This is surprising, since in the absence of additives, Celcon is more thermally stable. The temperature at which 90% volatilization has occurred for Celcon and Delrin are 442°C and 412°C , respectively, in a nitrogen atmosphere at a $15^\circ\text{C}/\text{min.}$ heating rate. It will be shown later that some additives have a more pronounced effect on Delrin than Celcon.

Effect of Oxidizing Agents on Delrin and Celcon

Figure 13 shows the effects of permanganate, perchlorate and dichromate salts of potassium on the thermal decomposition of Delrin and Celcon. The decomposition order is $\text{MnO}_4^- > \text{ClO}_4^- > \text{Cr}_2\text{O}_7$. This is the order of decreasing oxidation potential and consequently, the order of decreasing acidity. Thus as the acidity of the anion and cation increases, the more effective the salt is for the thermal degradation of polyacetals. The oxidation potentials in acidic solutions are -1.5, -1.37, and -1.33 volts for the couples $\text{Mn(II)}-\text{Mn(VII)}$, $\text{Cl(I)}-\text{Cl(VII)}$ and $\text{Cr(III)}-\text{Cr(VII)}$, respectively. Potassium permanganate leaves the largest residue (5% at 400°C) and has much greater effect on the decomposition of Delrin than on Celcon.

Effect of Metal Acetylacetonates on Delrin and Celcon

Figure 14 shows the effect of metal acetylacetonates on the decomposition of Delrin and Celcon. The decomposition order is $\text{Fe}^{+3} > \text{Co}^{+2} > \text{Co}^{+3} > \text{Zn}^{+2}$. These additives have a more pronounced effect on Delrin than Celcon. Osawa (ref. 12) studied the effect of fourteen transition and alkaline earth metals of stearic acid on the oxidative degradation of isotactic polypropylene and found $\text{Co} \gg \text{Al} > \text{Zn}$, and for decomposition of tert-butyl hydroperoxide found $\text{Co} \gg \text{Fe} > \text{Zn} > \text{Al}$.

Effect of Ammonium Salts of Perchlorate, Sulfate, and Phosphate on Delrin

Figure 15 shows the order $\text{NH}_4\text{ClO}_4 > (\text{NH}_4)_2\text{SO}_4 > (\text{NH}_4)_2\text{HPO}_4$ in lowering the thermal decomposition of Delrin. Phosphate, sulfate, and perchlorate are isosteric groups and are members of the third period. As you go across this period for this series, there is an increase in electronegativity of the non-metal and hence, an increase in acid strength of the anion and therefore the more effective it is as an additive in decreasing the thermal stability of Delrin.

Effect of Potassium Salts on Delrin

Figure 16 shows the order $\text{K}_2\text{S}_2\text{O}_8 \gg \text{KClO}_4 > \text{KClO}_3 > \text{K}_2\text{Cr}_2\text{O}_7 > \text{K}_2\text{SO}_4$ in decreasing the thermal stability of Delrin. There are at least three observations that can be made: (1) perchlorate is more effective than chlorate because the presence of an additional oxygen atom causes chlorine to be more positive (i.e. higher oxidation

state) thereby decreasing its ionic radius, and consequently increasing the acid strength of the anion; (2) perchlorate is more effective than sulfate because the chlorine is more electronegative and therefore increases the acid strength of the anion; (3) peroxydisulfate is much more effective than sulfate or perchlorate, probably because when it is heated, the peroxide linkage between the sulfur atoms breaks and liberates free radicals and oxygen which has a large catalytic effect on the decomposition of acetals; in comparison, potassium dichromate with seven oxygen atoms is not as effective an additive as potassium peroxydisulfate with eight oxygen atoms because the chromium atoms are linked together with a single oxygen, and consequently do not liberate oxygen or free radicals when heated; potassium dichromate is about as effective as potassium chlorate.

Effect of Persulfate and Perchlorate Salts on Delrin

Figure 17 shows the order $(\text{NH}_4)_2\text{S}_2\text{O}_8 > \text{NH}_4\text{ClO}_4 > \text{K}_2\text{S}_2\text{O}_8 \gg \text{KClO}_4$ on lowering the thermal decomposition of Delrin. This order indicates that (1) the more acid the character of the cation and anion, the more effective they are as additives, and (2) persulfates liberate free radicals and oxygen which can catalyze the decomposition reaction. It is evident that the effect on Delrin in going from $\text{K}_2\text{S}_2\text{O}_8$ to $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is small compared to going from KClO_4 to NH_4ClO_4 . DSC showed that the exothermic peak in $\text{K}_2\text{S}_2\text{O}_8$ corresponding to the exotherm in $(\text{NH}_4)_2\text{S}_2\text{O}_8$ came at a higher temperature (290°C).

Effect of Ammonium Salts of Perchlorate and Chloride on Delrin

Figure 18 shows the order $\text{NH}_4\text{ClO}_4 > \text{NH}_4\text{Cl} > (\text{CH}_3)_4\text{NClO}_4 > (\text{CH}_3)_4\text{NCl}$ in decreasing the thermal stability of Delrin. This order provides additional support for the conclusions drawn earlier, that the more acid character the cation and anion have, the more effective it is in decreasing the thermal stability of polyacetals. Perchlorate is more effective than chloride because the presence of oxygen atoms makes chlorine more positive and hence increases its acid strength. Methyl groups are base strengthening, consequently tetramethylammonium is more basic than ammonium and therefore less effective.

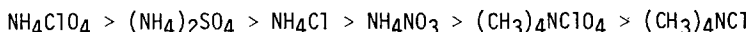
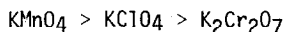
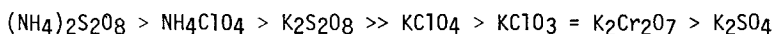
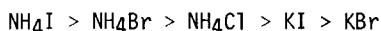
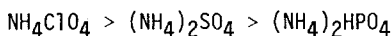
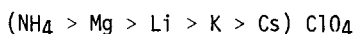
The admixture Delrin + NH_4NO_3 was also run. In comparing the effect of ammonium salts of perchlorate, sulfate chloride, and nitrate on decreasing the thermal stability of Delrin, the order was $\text{NH}_4\text{ClO}_4 > (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{Cl} > \text{NH}_4\text{NO}_3$. This is the order of decreasing acidity; the acidity functions (H_0) for the corresponding acids are -2.84, -2.76, -2.12, and -1.79 respectively (ref. 13).

The rate of volatilization of these additives with Delrin at 355°C is given in Table 11. In nitrogen the order is the same as observed by dynamic TG in nitrogen. However, in air the order is different, namely $\text{NH}_4\text{ClO}_4 = (\text{NH}_4)_2\text{SO}_4 > \text{NH}_4\text{NO}_3 > \text{NH}_4\text{Cl}$.

CONCLUSIONS

The rate of volatilization of seven polymers with/without 2 to 5% energetic additives has been determined by isothermal and dynamic thermogravimetry in a nitrogen and air atmosphere. Activation energies were determined for the thermal decomposition of some of the admixtures; the additives were found to lower the activation energy by 30 to 88%. Based on thermal analysis data only Delrin, Celcon, and Lucite showed promise as a possible consumable cartridge case.

The effect of a series of ammonium and potassium salts at the 2% level on the thermal decomposition of polyacetals was investigated by dynamic thermogravimetry. A general observation was that the more acid character the cation and anion had, then the more effective the additive was in lowering the decomposition temperature of the polyacetal. These observations were based on the following facts:



In addition the effect of organic additives yielding radicals had on the thermal degradation of Delrin was determined. The more effective additives had exotherms in the melting region of Delrin.

Our studies indicated that dynamic thermogravimetry offers a novel method for distinguishing between the acid strength of many inorganic compounds by the measurement of the shift of the TG curve of the Delrin admixture to lower temperature

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Table 1
ACTIVATION ENERGIES FOR THERMAL DECOMPOSITION OF
POLYMERS WITH/WITHOUT ADDITIVES

Sample in N ₂ atm	Activation Energy, kcal/mole	% Change in E _a
Celcon	37.8	
Celcon + APS ¹	4.5	88
Celcon + PNC ²	9.4	75
Lucite	25.2	
Lucite + AP ³	7.4	71
Lucite + NH ₄ Cl	17.9	30
AP ³	25.8	

¹APS is ammonium persulfate

²PNC is plastisol nitrocellulose

³AP is ammonium perchlorate

Table 2
COMPARISON OF RATE OF VOLATILIZATION OF POLYMERS AT 355 °C IN N₂ AND AIR

% V ⁽¹⁾	Nitrogen						
	Delrin RV ⁽²⁾	Celcon RV	Hytrel RV	Valox RV	Lucite RV	Nylon 4 RV	Nylon 612 RV
5	3.8	1.4	0.7	0.7	3.5	3.4	0.1
10	6.1	1.7	0.9	1.0	4.5	6.2	0.1
20	10.0	1.8	1.1	1.4	5.6	11.1	—
30	12.7	1.8	1.2	1.6	5.9	15.1	—
40	14.8	1.6	1.3	1.7	5.9	18.5	—
50	16.4	1.4	1.4	1.8	5.7	21.4	—
60	17.5	1.2	1.3	1.7	5.2	23.5	—
70	17.7	1.0	1.2	1.6	4.5	25.4	—
80	16.6	0.8	1.1	1.4	3.7	26.1	—
90	13.8	—	0.8	1.0	2.6	25.4	—
95	10.8	—	—	—	1.8	23.8	—
	Air						
5	5.8	6.9	2.9	1.3	4.3	3.7	0.2
10	11.4	13.5	5.4	1.8	8.5	6.7	0.2
20	22.2	26.7	5.5	2.4	16.5	11.7	—
30	32.6	39.5	11.5	2.8	24.8	15.7	—
40	42.6	51.2	9.2	3.1	32.8	19.0	—
50	52.1	61.7	7.1	3.2	40.3	21.5	—
60	61.2	71.4	4.9	3.2	48.0	23.3	—
70	70.0	80.5	3.5	3.1	55.1	24.6	—
80	76.9	89.4	2.4	2.7	62.0	25.2	—
90	84.1	97.8	—	1.5	68.2	24.7	—
95	86.4	101.1	—	—	70.9	23.3	—

(1) V is volatilization

(2) RV is rate of volatilization, % per minute.

Table 3
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF DELRIN
AT 355 °C IN NITROGEN AND AIR

Nitrogen							
% V ⁽⁷⁾	Delrin + RV ⁽⁸⁾	5.1% APS RV ⁽¹⁾	4.4% AP RV ⁽²⁾	4.7% HMX RV ⁽³⁾	4.6% TAGN RV ⁽⁴⁾	4.5% PNC RV ⁽⁵⁾	~4% BLC RV ⁽⁶⁾
5	3.8	15.6	14.3	6.0	9.3	21.7	7.1
10	6.1	25.0	25.0	10.5	10.2	34.5	11.8
20	10.0	38.5	42.6	17.1	18.4	51.3	17.4
30	12.7	48.4	54.6	21.9	20.6	60.0	20.8
40	14.8	56.3	66.7	25.2	21.7	66.7	22.9
50	16.4	63.3	71.4	27.2	22.1	71.4	23.3
60	17.5	68.2	80.0	28.3	21.6	75.9	21.7
70	17.7	72.9	82.4	29.2	20.2	79.6	18.2
80	16.6	76.2	88.9	30.1	17.7	82.5	13.9
90	13.8	76.3	90.0	25.6	14.1	83.3	8.2
Air							
5	5.8	20.8	25.0	8.9	6.4	12.5	7.1
10	11.4	30.3	45.4	15.2	10.2	21.7	12.8
20	22.2	51.3	80.0	25.0	17.0	39.2	22.5
30	32.6	62.5	103.4	32.6	24.4	56.6	31.9
40	42.6	72.7	117.6	41.2	32.0	74.1	42.1
50	52.1	82.0	119.1	51.0	39.4	89.3	51.5
60	61.2	93.8	115.4	58.8	46.5	103.4	60.0
70	70.0	104.5	112.9	66.7	53.4	114.8	68.0
80	76.9	114.3	111.1	73.4	59.3	125.0	75.5
90	84.1	123.3	107.1	79.0	49.4	132.4	81.8

(1) APS is ammonium persulfate

(2) AP is ammonium perchlorate

(3) HMX is cyclotetramethylenetetranitramine

(4) TAGN is triaminoguanidine nitrate

(5) PNC is plastisol nitrocellulose

(6) BLC is black lacquer coating

(7) % V is percent volatilization

(8) RV is rate of volatilization in percent per minute

Table 4
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF CELCON
AT 355 °C IN NITROGEN AND AIR

Nitrogen							
% V ⁽⁷⁾	Celcon + RV ⁽⁸⁾	4.8% APS RV ⁽¹⁾	5.0% AP RV ⁽²⁾	4.6% HMX RV ⁽³⁾	4.6% TAGN RV ⁽⁴⁾	4.1% PNC RV ⁽⁵⁾	~4% BLC RV ⁽⁶⁾
5	1.4	19.2	23.8	6.0	12.5	8.3	8.3
10	1.7	29.4	40.0	10.0	10.5	12.5	16.1
20	1.8	45.4	64.5	13.3	6.7	17.4	24.7
30	1.8	55.6	83.3	13.8	4.0	18.9	25.0
40	1.6	65.6	93.0	11.1	2.8	18.6	22.9
50	1.4	73.5	102.0	5.2	2.1	16.7	17.5
60	1.2	79.0	109.1	3.1	1.7	13.1	11.8
70	1.0	85.4	112.9	2.1	1.4	9.5	7.6
80	0.8	88.9	117.6	1.5	1.1	—	4.6
90	—	92.8	118.4	—	—	—	2.2
Air							
5	6.9	29.4	10.9	9.3	8.3	7.6	10.0
10	13.5	45.4	21.8	16.1	10.6	12.2	17.5
20	26.7	64.5	40.8	26.3	16.1	21.5	22.2
30	39.5	79.0	58.8	35.7	23.1	30.6	25.0
40	51.2	87.0	75.5	45.4	29.8	39.2	26.7
50	61.7	94.3	89.3	55.6	37.0	48.1	32.5
60	71.4	100.0	96.8	65.2	44.1	56.6	36.4
70	80.6	104.5	100.0	73.7	50.7	64.8	41.7
80	89.4	108.1	101.3	82.5	56.7	72.1	45.2
90	97.8	109.8	100.0	90.0	62.9	79.0	—

(1) APS is ammonium persulfate

(2) AP is ammonium perchlorate

(3) HMX is cyclotetramethylenetetranitramine

(4) TAGN is triaminoguanidine nitrate

(5) PNC is plastisol nitrocellulose

(6) BLC is black lacquer coating

(7) % V is percent volatilization

(8) RV is rate of volatilization in percent per minute

Table 5
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF HYTREL
AT 355°C IN NITROGEN AND AIR

Nitrogen							
% V(7)	Hytrel + RV(8)	4.3% APS RV(1)	4.9% AP RV(2)	4.4% HMX RV(3)	4.6% TAGN RV(4)	4.7% PNC RV(5)	~4% BLC RV(6)
5	0.7	6.2	4.5	5.3	1.3	2.5	10.4
10	0.9	10.0	8.2	1.8	1.0	1.5	20.0
20	1.1	14.3	16.7	1.6	1.2	1.6	35.7
30	1.2	4.4	10.0	1.7	1.4	1.7	8.7
40	1.3	3.3	3.8	1.7	1.45	1.7	4.3
50	1.4	2.8	2.9	1.6	1.4	1.6	2.3
60	1.3	2.5	2.4	1.5	1.3	1.5	1.7
70	1.2	2.1	2.0	1.4	1.2	1.4	1.2
80	1.1	1.8	1.6	—	—	1.2	—
90	0.8	—	—	—	—	—	—
Air							
5	2.9	5.6	6.7	7.1	5.2	4.5	10.2
10	5.4	10.5	12.2	8.4	5.7	6.9	20.0
20	5.5	20.0	20.0	10.0	6.4	11.9	39.2
30	11.5	15.0	15.0	9.1	5.5	13.6	25.0
40	9.2	10.3	7.8	7.7	4.8	9.5	14.3
50	7.1	7.6	6.0	6.3	4.2	7.0	1.7
60	4.9	5.9	5.0	5.2	3.7	6.5	—
70	3.5	4.7	4.2	4.1	3.1	4.3	—
80	2.4	3.5	3.2	2.8	2.3	3.0	—
90	—	—	—	—	—	—	—

(1) APS is ammonium persulfate

(2) AP is ammonium perchlorate

(3) HMX is cyclotetramethylenetetranitramine

(4) TAGN is triaminoguanidine nitrate

(5) PNC is plastisol nitrocellulose

(6) BLC is black lacquer coating

(7) % V is percent volatilization

(8) RV is rate of volatilization in percent per minute

Table 6
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF VALOX
AT 355°C IN NITROGEN AND AIR

Nitrogen							
% V(7)	Valox + RV(8)	5.1% APS RV(1)	4.6% AP RV(2)	4.8% HMX RV(3)	4.7% TAGN RV(4)	4.5% PNC RV(5)	4% BLC RV(6)
5	0.7	1.7	2.6	1.3	1.3	1.3	8.6
10	1.0	1.6	2.5	1.2	1.2	1.2	16.4
20	1.4	1.8	2.2	1.4	1.6	1.3	8.3
30	1.6	1.9	2.4	1.6	1.7	1.4	3.8
40	1.7	1.9	2.5	1.65	1.75	1.5	2.8
50	1.8	1.9	2.4	1.6	1.8	1.55	2.2
60	1.7	1.8	2.3	1.5	1.7	1.5	1.8
70	1.6	1.7	2.0	—	1.6	1.4	1.3
80	1.4	1.5	1.7	—	1.3	—	—
90	1.0	—	—	—	—	—	—
Air							
5	1.3	1.8	2.6	2.8	2.1	2.2	10.0
10	1.8	2.2	2.7	2.5	2.3	2.3	14.9
20	2.4	2.8	2.8	2.9	2.9	2.8	6.8
30	2.8	3.2	3.1	3.3	3.4	3.1	4.2
40	3.1	3.25	3.3	3.5	3.6	3.3	4.0
50	3.2	3.35	3.35	3.6	3.7	3.35	3.7
60	3.2	3.3	3.2	3.6	3.6	3.3	3.0
70	3.1	3.1	3.0	3.4	3.5	3.1	—
80	2.7	2.8	2.6	3.1	3.0	2.7	—
90	1.5	1.7	—	2.5	—	1.5	—

(1) APS is ammonium persulfate

(2) AP is ammonium perchlorate

(3) HMX is cyclotetramethylenetetranitramine

(4) TAGN is triaminoguanidine nitrate

(5) PNC is plastisol nitrocellulose

(6) BLC is black lacquer coating

(7) % V is percent volatilization

(8) RV is rate of volatilization in percent per minute

Table 7
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF LUCITE
AT 355 °C IN NITROGEN AND AIR

Nitrogen							
% V ⁽⁷⁾	Lucite + RV ⁽⁸⁾	5.0% APS RV ⁽¹⁾	4.5% AP RV ⁽²⁾	4.9% HMX RV ⁽³⁾	5.4% TAGN RV ⁽⁴⁾	5.2% PNC RV ⁽⁵⁾	~4% BLC RV ⁽⁶⁾
5	3.5	3.6	6.6	4.9	7.6	5.8	5.2
10	4.5	4.4	11.6	8.5	10.2	5.4	7.1
20	5.6	5.0	20.0	14.3	14.1	4.5	6.1
30	5.9	5.0	27.0	16.7	12.5	4.3	5.2
40	5.9	4.9	32.8	16.5	9.1	4.0	4.3
50	5.7	4.4	37.0	11.9	6.8	3.6	3.7
60	5.2	3.9	39.7	7.9	5.2	3.2	3.2
70	4.5	3.3	40.7	5.0	4.0	2.7	2.9
80	3.7	2.5	38.6	3.0	2.8	2.2	2.5
90	2.6	1.5	20.9	1.6	1.6	1.5	2.2
Air							
5	4.3	61	77	60	93	46.7	8.5
10	8.5	105	141	105	132	86.2	12.0
20	16.5	194	247	189	208	167	18.2
30	24.8	275	333	273	291	248	26.5
40	32.8	354	404	354	364	317	34.8
50	40.3	417	472	427	439	385	43.1
60	48.0	476	536	500	504	451	50.8
70	55.1	522	582	569	574	504	58.3
80	62.0	559	667	635	635	559	65.6
90	68.2	600	714	692	692	604	72.6

(1) APS is ammonium persulfate
(2) AP is ammonium perchlorate
(3) HMX is cyclotetramethylenetetranitramine
(4) TAGN is triaminoguanidine nitrate
(5) PNC is plastisol nitrocellulose
(6) BLC is black lacquer coating
(7) % V is percent volatilization
(8) RV is rate of volatilization in percent per minute

Table 8
EFFECT OF ADDITIVES ON THE RATE OF VOLATILIZATION OF NYLON-4
AT 355 °C IN NITROGEN AND AIR

Nitrogen							
% V ⁽⁷⁾	Nylon-4 + RV ⁽⁸⁾	4.6% APS RV ⁽¹⁾	5.0% AP RV ⁽²⁾	4.6% HMX RV ⁽³⁾	4.7% TAGN RV ⁽⁴⁾	4.5% PNC RV ⁽⁵⁾	~4% BLC RV ⁽⁶⁾
5	3.4	4.0	6.2	6.1	6.2	6.7	7.1
10	6.2	6.9	11.0	8.5	8.5	6.8	12.2
20	11.1	12.7	19.4	13.9	13.5	11.7	13.8
30	15.1	16.6	26.8	18.2	17.5	15.8	17.1
40	18.5	20.5	33.3	21.5	20.6	19.0	19.8
50	21.4	23.8	38.8	23.9	23.1	21.6	21.7
60	23.5	26.7	43.5	26.0	25.0	23.5	23.0
70	25.4	29.0	47.3	27.2	26.3	25.0	23.1
80	26.1	30.2	49.1	27.6	26.9	25.8	26.4
90	25.4	29.3	45.0	26.5	26.4	25.4	
Air							
5	3.7	6.2	5.4	5.2	6.7	8.3	8.3
10	6.7	10.0	9.8	7.6	8.9	8.3	13.3
20	11.7	16.7	18.0	12.9	14.3	13.8	14.8
30	15.7	22.4	25.0	17.1	18.8	18.2	18.1
40	19.0	27.6	31.5	20.6	22.2	21.7	20.8
50	21.5	31.8	37.0	23.3	25.0	24.6	22.8
60	23.3	35.3	41.7	25.4	27.0	26.9	24.4
70	24.6	37.8	45.2	26.8	28.6	28.6	25.0
80	25.2	38.5	45.7	27.4	29.6	29.5	18.8
90	24.7	36.0	31.0	26.5	29.1	29.0	

(1) APS is ammonium persulfate
(2) AP is ammonium perchlorate
(3) HMX is cyclotetramethylenetetranitramine
(4) TAGN is triaminoguanidine nitrate
(5) PNC is plastisol nitrocellulose
(6) BLC is black lacquer coating
(7) % V is percent volatilization
(8) RV is rate of volatilization in percent per minute

Table 9
COMPARISON OF RATE OF VOLATILIZATION OF POLYMERS COATED
WITH BLACK LACQUER AT 355°C IN NITROGEN AND AIR

Nitrogen							
% V ⁽¹⁾	Delrin RV ⁽²⁾	Celcon RV	Hytrel RV	Valox RV	Lucite RV	Nylon 4 RV	Nylon 612 RV
5	7.1	8.3	10.4	8.6	5.2	7.1	9.1
10	11.8	16.1	20.0	16.4	7.1	12.2	17.9
20	17.4	24.7	35.7	8.3	6.1	13.8	33.9
30	20.8	25.0	8.7	3.8	5.2	17.1	20.7
40	22.9	22.9	4.3	2.8	4.3	19.8	8.3
50	23.3	17.5	2.3	2.2	3.8	21.7	3.0
60	21.7	11.8	1.7	1.8	3.2	23.0	0.7
70	18.2	7.6	1.2	1.3	2.9	23.1	—
80	13.9	4.6	—	—	2.5	26.4	—
90	8.2	2.2	—	—	2.2	—	—
Air							
5	7.1	10.0	10.2	10.0	8.5	8.3	10.0
10	12.8	17.5	20.0	14.9	12.0	13.3	18.2
20	22.5	22.2	39.2	6.8	18.2	14.8	33.3
30	31.9	25.0	25.0	4.2	26.6	18.1	23.1
40	42.1	26.7	14.3	4.0	34.8	20.8	15.1
50	51.5	32.5	1.7	3.7	43.1	22.8	2.1
60	60.0	36.4	—	3.0	50.8	24.4	1.1
70	68.0	41.7	—	—	58.3	25.0	1.0
80	75.5	45.2	—	—	65.6	18.8	0.9
90	81.8	—	—	—	72.6	—	0.7

(1) V is volatilization

(2) RV is rate of volatilization, % per minute.

Table 10
TEMPERATURE AT WHICH 80% DECOMPOSITION BY WEIGHT OCCURS
FOR DELRIN + ADDITIVES

Temperature, °C	a. Delrin + 2% Additives Additive
200	Ammonium persulfate
211	Ammonium perchlorate
230	Potassium persulfate
264	N-Bromosuccinimide ⁽¹⁾
330	Peracetic acid, 40%
341	Potassium perchlorate
351	N-Chlorosuccinimide ⁽¹⁾
353	Dicumyl peroxide
355	Azobutyronitrile
366	Dimethyl benzylamine
374	Benzoyl peroxide
380	1,3-Diphenyltriazen ⁽¹⁾
382	Paramethane hydroperoxide
388	Delrin alone
398	Tertiary butyl hydroperoxide, 70%
403	Tetramethyl thiuram disulfide ⁽¹⁾
	b. Delrin + 2% (NH ₄) ₂ S ₂ O ₈ + 2% Additive
178	N-Chlorosuccinimide
185	Azobutyronitrile
197	Dicumyl peroxide
200	Benzoyl peroxide
202	Tetramethyl thiuram disulfide
	c. Delrin + 2% NH ₄ ClO ₄ + 2% Additive
203	N-Chlorosuccinimide
216	Azobutyronitrile
218	Benzoyl peroxide
231	Dicumyl peroxide
231	Tetramethyl thiuram disulfide

(1) Two step TGA curve and two DSC decomposition peaks.

Table 11
EFFECT OF AMMONIUM SALTS ON THE RATE OF
VOLATILIZATION OF DELRIN
AT 355 °C IN NITROGEN AND AIR

Nitrogen					
% V ⁽¹⁾	Delrin RV ⁽²⁾	4.4 % NH ₄ C10 ₄	4.5 % (NH ₄) ₂ SO ₄	4.5 % NH ₄ C1	4.6 % NH ₄ NO ₃
5	3.8	14.3	10.9	10.4	6.2
10	6.1	25.0	20.4	15.8	10.0
20	10.0	42.6	34.5	23.8	15.4
30	12.7	54.6	45.5	29.7	18.7
40	14.8	66.7	52.6	33.9	20.0
50	16.4	71.4	59.5	37.3	20.7
60	17.5	80.0	65.2	39.5	18.6
70	17.7	82.4	70.0	41.2	14.5
80	16.6	88.9	73.4	41.7	11.1
90	13.8	90.0	76.3	40.9	7.7
Air					
5	5.8	25.0	11.9	11.4	7.7
10	11.4	45.4	23.3	19.2	12.7
20	22.2	80.0	44.4	29.0	23.3
30	32.6	103.4	65.2	35.7	34.1
40	42.6	117.6	85.2	41.2	44.4
50	52.1	119.1	104.2	45.4	54.3
60	61.2	115.4	120.0	48.8	63.8
70	70.0	112.9	137.3	51.1	72.9
80	76.9	111.1	150.9	51.9	80.8
90	84.1	107.1	160.7	52.1	89.1

(1) % V is percent volatilization

(2) RV is rate of volatilization in percent per minute

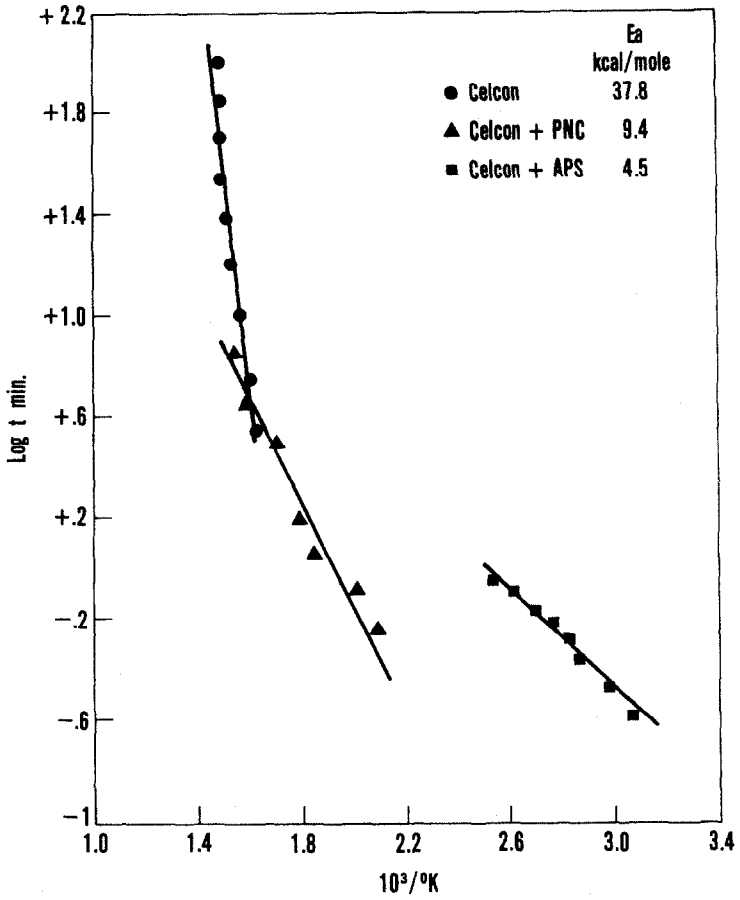


Figure 1. ACTIVATION ENERGY PLOT FOR CELCON AND CELCON + ADDITIVES

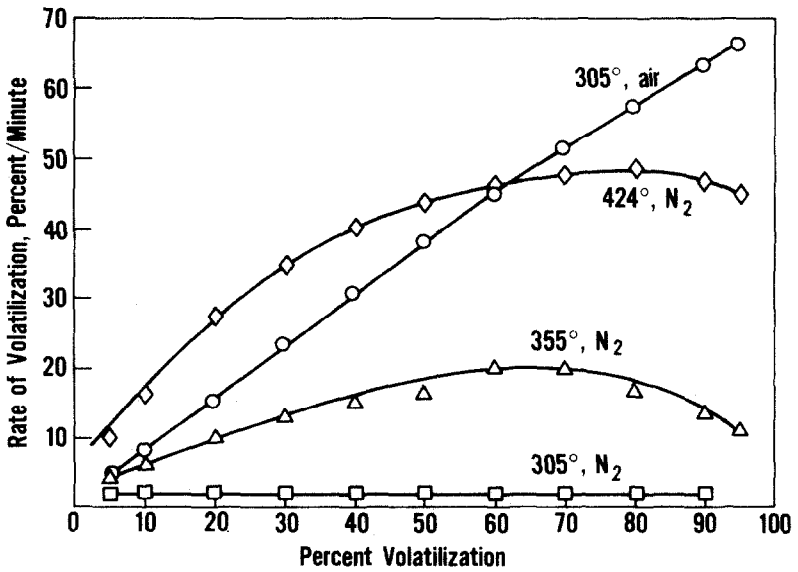


Figure 2. RATE OF VOLATILIZATION OF DELRIN IN N₂ AND AIR

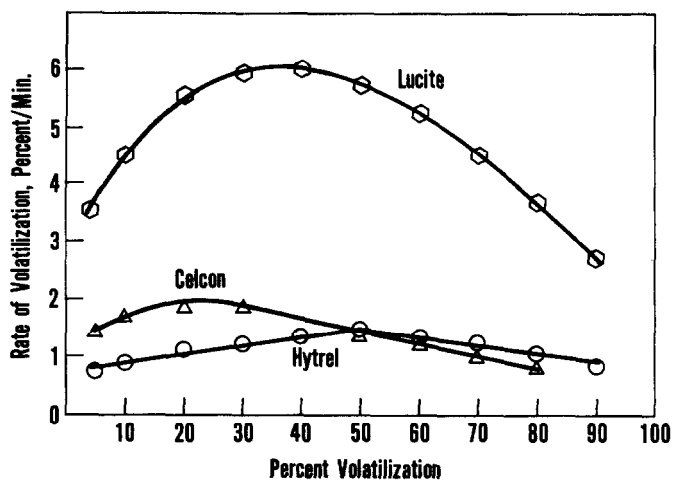


Figure 3. RATE OF VOLATILIZATION OF POLYMERS IN NITROGEN AT 355°C

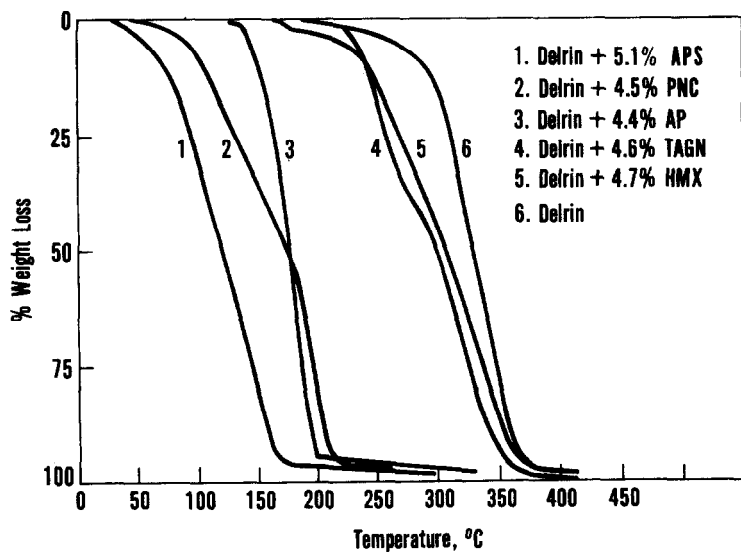


Figure 4. EFFECT OF ADDITIVES ON THE DEGRADATION OF DELRIN IN NITROGEN AT 5°C/MINUTE

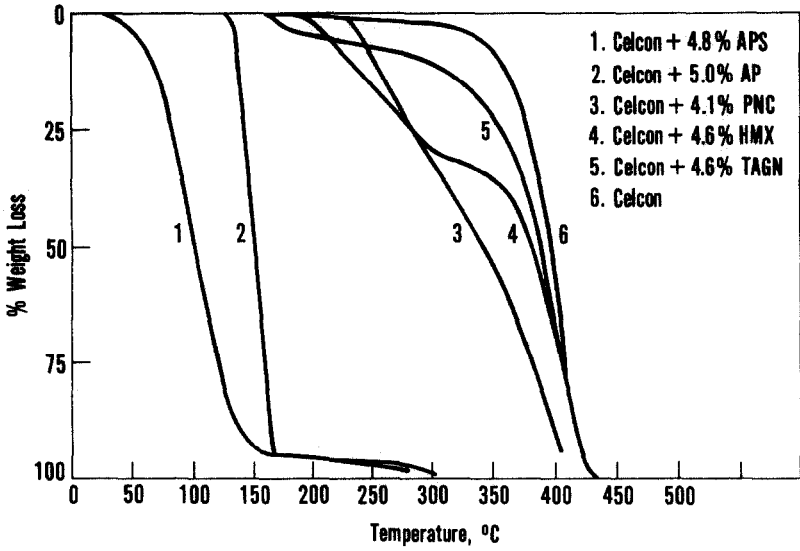


Figure 5. EFFECT OF ADDITIVES ON THE DEGRADATION OF CELCON IN NITROGEN AT 5°C/MINUTE

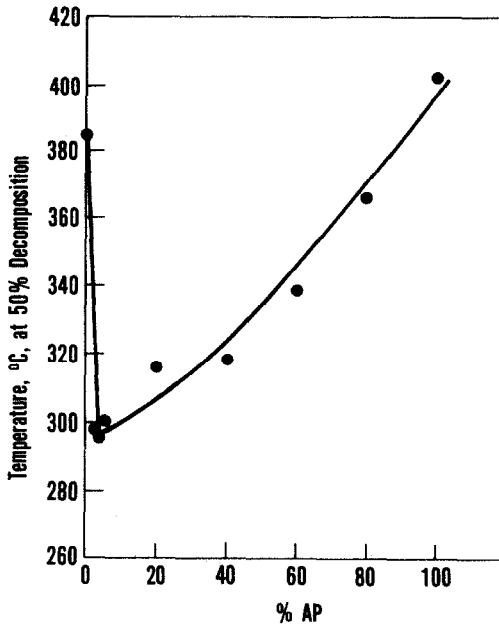


Figure 6. EFFECT OF AP CONCENTRATION ON THE THERMAL DECOMPOSITION OF A MIXTURE OF LUCITE + AP

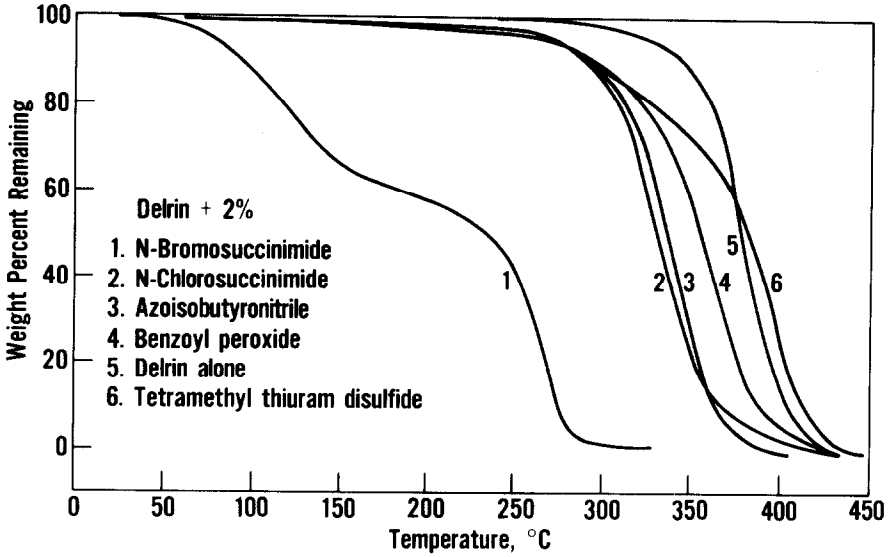


Figure 7. EFFECT OF FREE RADICAL INITIATORS ON THE THERMAL DECOMPOSITION OF DELRIN

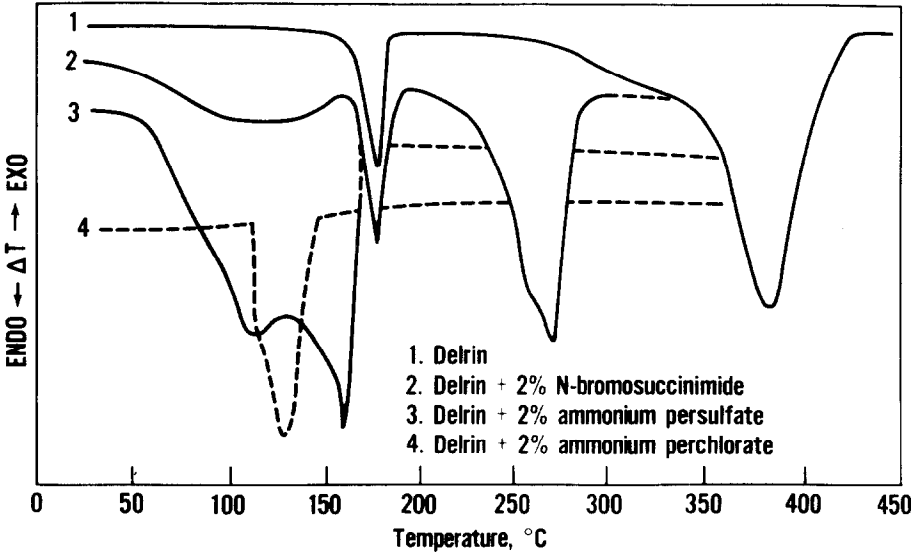


Figure 8. DSC OF DELRIN AND DELRIN + ADDITIVES

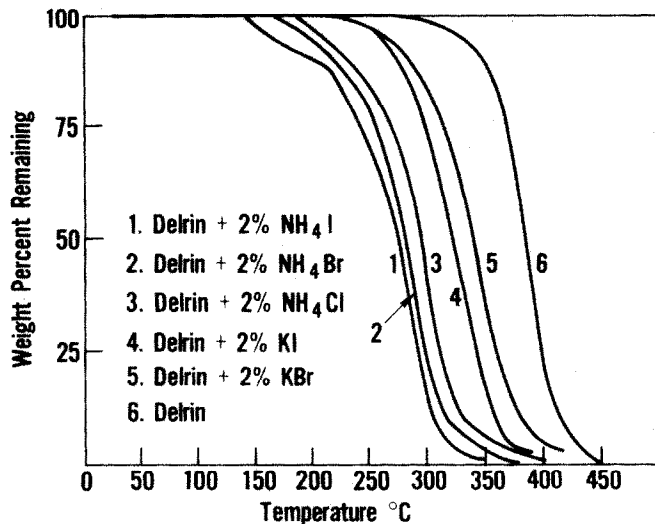


Figure 9. EFFECT OF AMMONIUM AND POTASSIUM HALIDES ON THE THERMAL DECOMPOSITION OF DELRIN

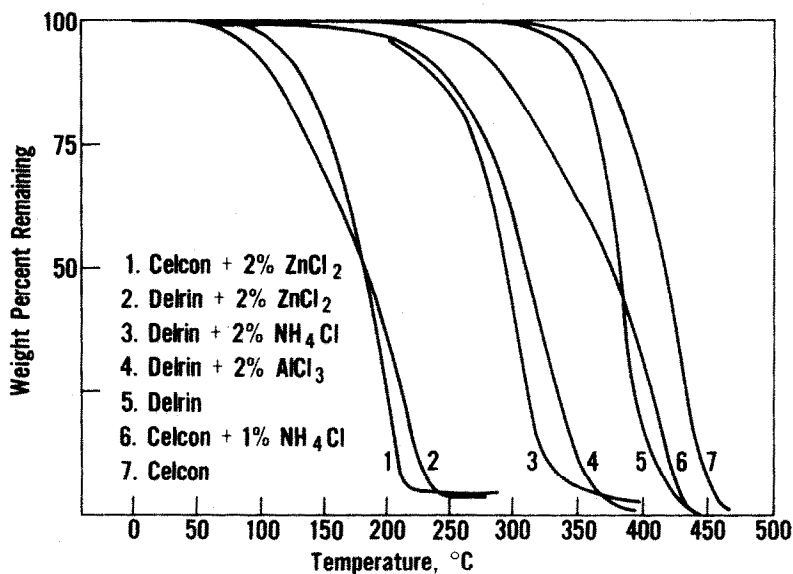


Figure 10. EFFECT OF CHLORIDE SALTS ON DECOMPOSITION OF DELRIN AND CELCON IN A NITROGEN ATMOSPHERE

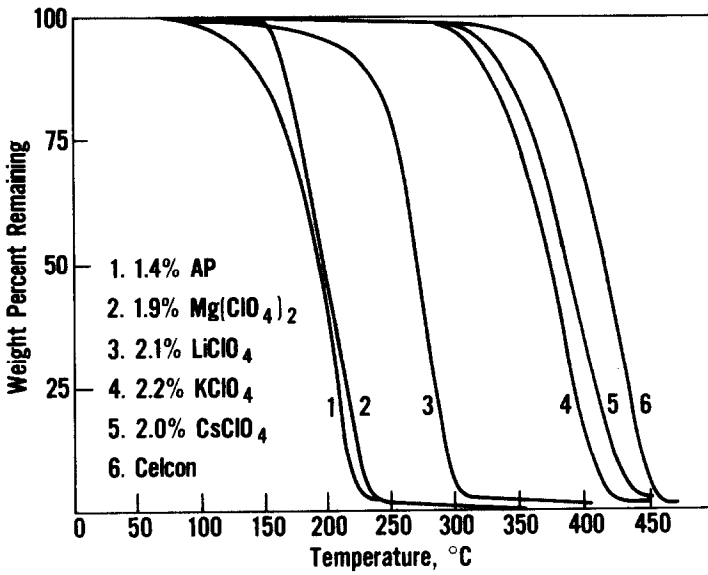


Figure 11. EFFECT OF PERCHLORATE SALTS ON DECOMPOSITION OF CELCON IN A NITROGEN ATMOSPHERE

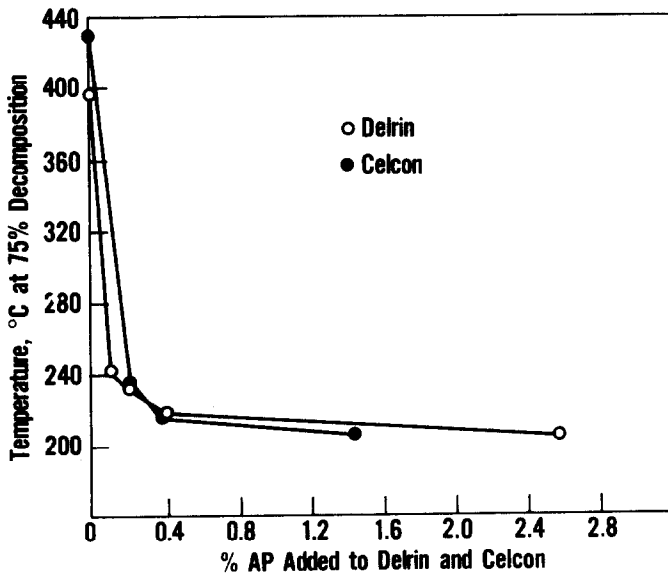


Figure 12. LIMITING EFFECT OF AP CONCENTRATION ON DECOMPOSITION OF DELRIN AND CELCON IN A NITROGEN ATMOSPHERE

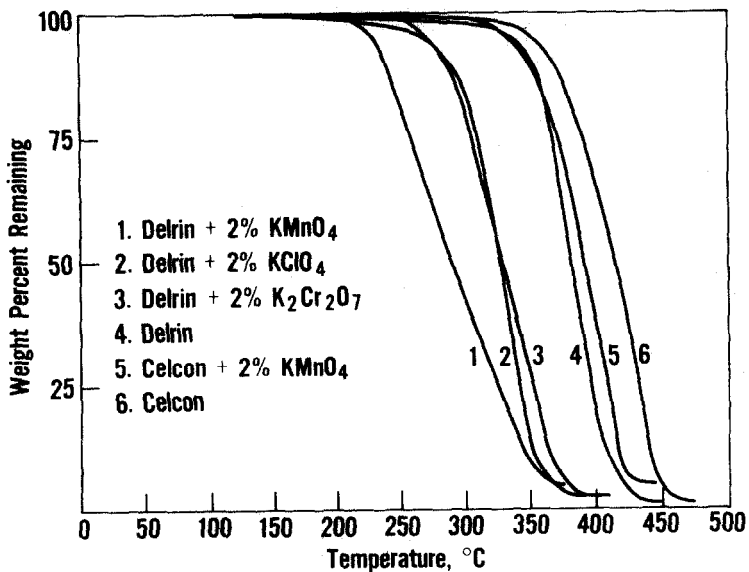


Figure 13. EFFECT OF OXIDIZING AGENTS ON DECOMPOSITION OF DELRIN AND CELCON IN A NITROGEN ATMOSPHERE

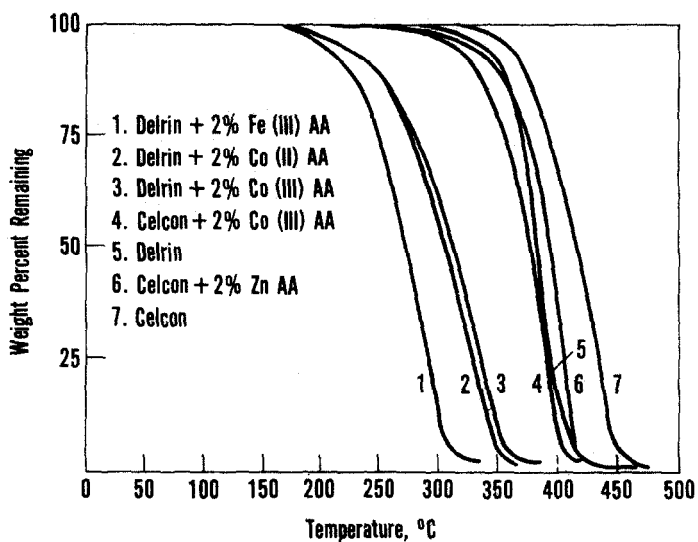


Figure 14. EFFECT OF METAL ACETYLACETONATES ON DECOMPOSITION OF DELRIN AND CELCON IN A NITROGEN ATMOSPHERE

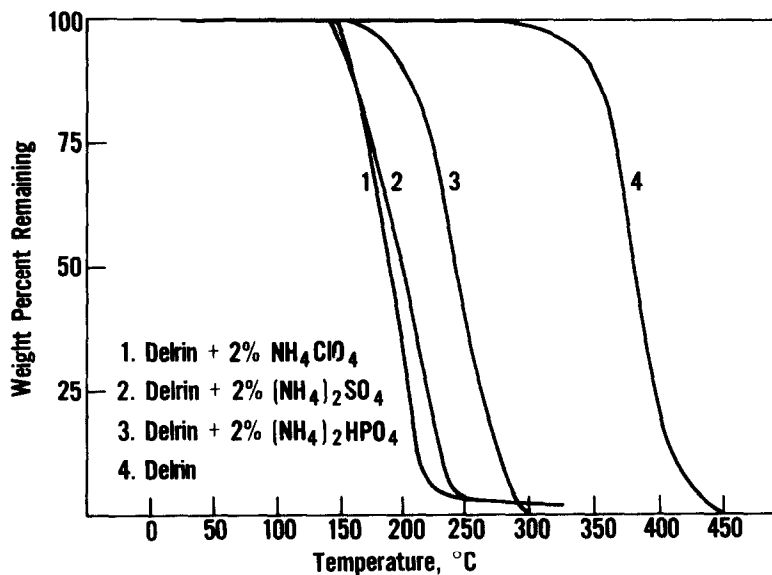


Figure 15. EFFECT OF PERCHLORATE, SULFATE AND PHOSPHATE AMMONIUM SALTS ON THERMAL DECOMPOSITION OF DELRIN

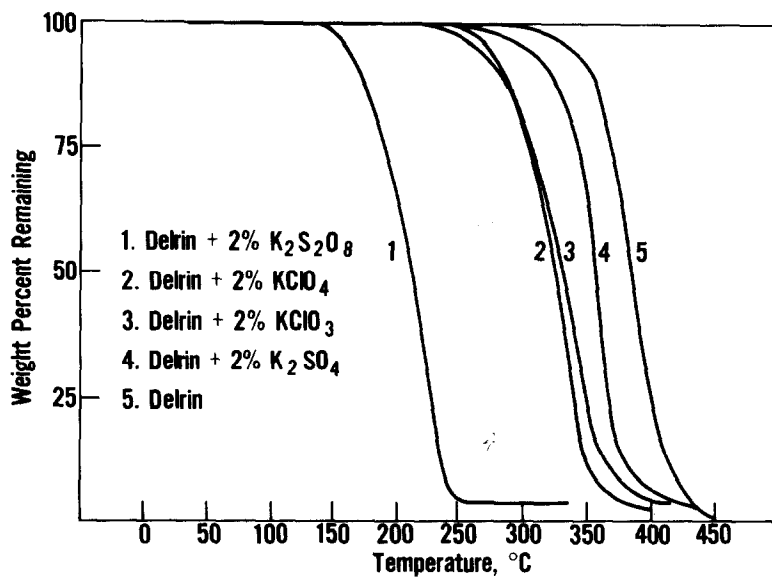


Figure 16. EFFECT OF CHLORATE, PERCHLORATE, SULFATE AND PEROXYDISULFATE POTASSIUM SALTS ON THERMAL DECOMPOSITION OF DELRIN

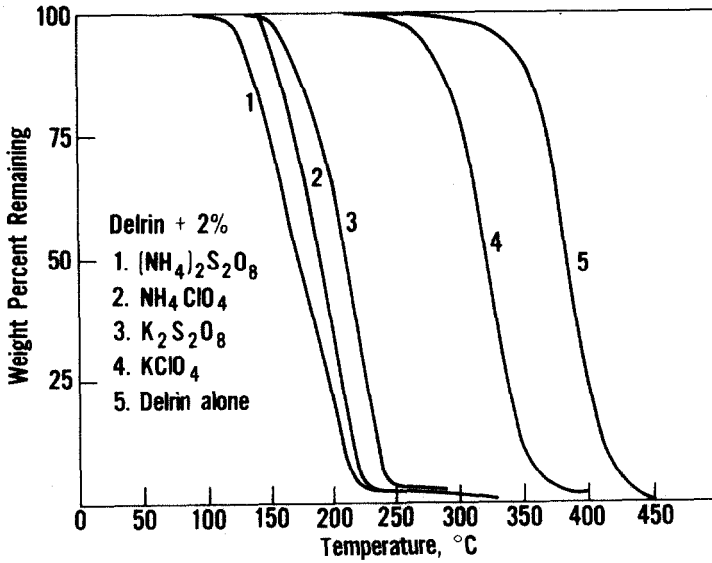


Figure 17. EFFECT OF AMMONIUM AND POTASSIUM SALTS OF PERSULFATE AND PERCHLORATE ON THERMAL DECOMPOSITION OF DELRIN

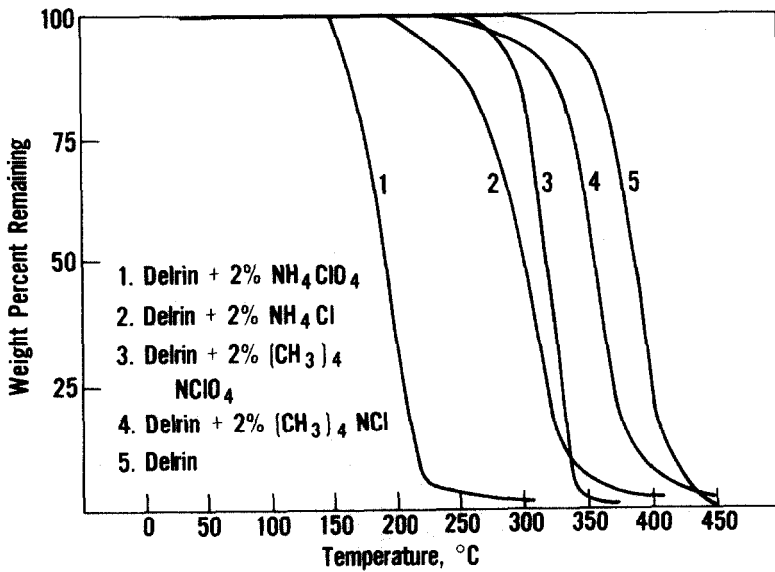


Figure 18. EFFECT OF TWO AMMONIUM PERCHLORATES AND CHLORIDES ON THE THERMAL DECOMPOSITION OF DELRIN